

Status Report

DEVELOPMENT OF SURFACTANTS AS PROFILE MODIFICATION AGENTS

By David K. Olsen

Project OE3, Milestone 2, FY88

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SUMMARY

This report summarizes a scoping study conducted during FY87 and FY88 on the "Development of Surfactants as Profile Modification Agents," Project OE3, and completes all tasks under this program. This status report outlines accomplishments and necessary steps required to advance the system.

Proprietary amine oxide surfactants manufactured by Akzo Chemicals Inc. (PF1 through PF9) were evaluated in a scoping study to determine their potential as fluid diversion agents (profile modification) for application in waterfloods to increase sweep efficiency and thus increase oil recovery. In-depth fluid diversion was shown in 40-ft parallel Monel slim tube experiments as well as in parallel 1- and 4-ft Berea sandstone cores. The amine oxide-alcohol surfactant system was designed so that the system would separate and leave a viscous gel to plug pore throats in high-permeability zones. Water was then diverted to lower permeability zones and sweep efficiency and oil production were increased.

The chemical system was based on the chromatographic separation and/or phase partitioning of an amine oxide-alcohol blend. The alcohol in the blend was selected to either transport faster than or slower than the surfactant so that the two components separated. The PF series of surfactants yielded viscous gels when separated from the alcohol that blocked pore throats in the rock matrix and thus caused a fluid diversion.

Most of the screening work was directed toward the evaluation of PF2 (containing isopropyl alcohol and water) or PF4 (containing only water) based upon the cost of the surfactant and the performance of the materials. The hydrogenated versions of these surfactants, PF1 and PF7, are expected to behave equally well, but their cost is higher. Samples of PF3 and PF6 failed to yield solutions that have adequate viscosity. Sample PF5 had solution behavior that may limit its application. PF9 showed solution behavior that limits its application for profile modification, and sample PF8 has not been evaluated but should be an ideal candidate based upon price and performance of similar analogues. Future work should concentrate on PF8.

The amine oxide-alcohol system shows promise for use in fluid diversion; however, additional work must be undertaken to reduce the concentration of materials, define the sequence of how to place a block at 50, 100, or 150 ft as desired, and better define the limitations of the system.

BACKGROUND

Reservoir heterogeneities and variations in permeability affect sweep efficiencies of displacing fluids. Oil recovery efficiency is the product of microscopic displacement efficiency and volumetric sweep efficiency (both areal sweep and vertical sweep). When inexpensive fluids such as water are used, a lower sweep efficiency can be tolerated, but as the water-to-oil ratio increases or more costly enhanced oil recovery (EOR) fluids are used, steps must be initiated to improve the sweep efficiency. Small improvements in volumetric sweep efficiency can have a large effect on the overall efficiency and economics of an oil recovery process. Gelled polymers are often used for profile modification treatments but usually do not achieve in-depth penetration into the formation. A system that achieves in-depth plugging of highly permeable zones in reservoirs would greatly improve the effectiveness of profile modification treatments. Profile modification by injection of a low-viscosity mixture of surfactant and alcohol would have the advantage of providing good injectivity and potentially could result in in-depth penetration into formations.

Poor distribution of injected fluids arises from differences in the viscosity of the fluids (viscous fingering) and reservoir heterogeneities. Water flows through zones of higher permeability (due to geology or high water saturation) and bypasses zones of lower permeability leaving much of the reservoir unswept. Additional injected water recovers little additional oil, and the producing water-oil ratio increases until an economic limit is reached and the well is abandoned. Significant advances in technology to reduce flow through high-permeability zones have been made during the past decade. Field application of gelled polymers is one method that has proved to be a cost-effective way to divert fluids, but this process is not without constraints. The reaction of polymer and crosslinker is temperature- and time-dependent, making the placement of effective barriers at greater distances away from the well more difficult. There are unanswered questions about the long-term

stability of gels and how to treat gels that have failed or have crossflow (fluid diversion) around a barrier such that the fluid is flowing through the original channel. Near-wellbore, profile-improvement techniques call for both biopolymers and polyacrylamides as the principal polymers and a trivalent ion such as chromium as the crosslinker.

An alternate technique of profile improvement has used sequential injection of a cationic polymer and a water spacer, followed by an anionic polymer; the sequence is repeated a number of times so that flow is reduced in the high-permeability zones. Both techniques have performed with mixed success in field applications. Improvements have been made in both the products and the method of application. Some systems are being used routinely in certain fields.

There continues to be uncertainty in applications of diverting agents since operators do not know how long the treatment will last, how far the barrier is placed away from the well, or whether polymer will be produced. Some operators have plugged off wells and have been unsuccessful in returning them to production. Small operators who cannot afford the costs of bringing a pump truck and mixer on location face an additional constraint. An ideal situation would provide a profile-improvement agent that could be added to the injection fluid so that the fluid would have a viscosity similar to that of the brine being used in a waterflood.

OBJECTIVE

The objective of this work was to provide scoping studies develop a profile-modification technique that will provide in-depth preferential penetration into highly permeable zones that have been swept by water and thus provide improved sweep efficiency.

SCOPE OF WORK

This program was designed to develop a profile-modification agent consisting of a surfactant-alcohol blend which initially has a low viscosity, but where the surfactant alone has a very high viscosity. Thus, wellhead-injection pressures will remain relatively constant while the slug is injected. The slug will follow high-permeability streaks and be displaced deep into the reservoir. As the slug propagates, the reservoir rock causes

the alcohol and surfactant components to separate leaving the highly viscous surfactant gel to block the pores, thus reducing the flow of fluid through that channel. The alcohol which has separated from the surfactant will diffuse into the surrounding fluid. Separation of alcohol from surfactant may be caused by the following: differences in relative adsorption of the alcohol surfactant; chromatographic separation of the surfactant-alcohol blend; or differences in the hydrophobicity of the blend, resulting in the components partitioning to different extents into the aqueous phase and oleic phase. The depth of penetration of the surfactant can be varied by adjusting the type and amount of alcohol in the formulation.

Selection of surfactant and alcohol may be dependent upon the temperature and salinity of the reservoir as well as the oil composition. Surfactant slug formulation, ratio of components, and the size of the slug were investigated.

This study was limited to a screening or scoping study to demonstrate the feasibility of the process and was not intended to be comprehensive enough to necessarily define optimum conditions.

The original work plan¹ for this project is shown in the accompanying tasks.

Task 1 - Selection of surfactant candidates and test conditions. (Start date: Feb. 1, 1987. Completion date: Feb. 10, 1987.)

The initial selection of surfactants will be from amine oxides and water soluble alcohols such as isopropyl or isobutyl alcohol. The test conditions will simulate North Burbank field (Oklahoma), site of a previous DOE-industry cost-shared chemical flood field demonstration.

Task 2 - Screen surfactants at reservoir conditions and determine viscosity relationships. (Start date: Feb. 10, 1987. Completion date: Mar. 1, 1987.)

A minimum number of surfactant-alcohol blends will be screened. Screening of the surfactant-alcohol blend will include determination of changes in viscosity with changes in alcohol concentration and determination of phase-inversion temperature(s) of crude oil-surfactant-alcohol blends.

Task 3 - Conduct corefloods to establish blocking efficiency. (Start date: Mar. 1, 1987. Completion date: Apr. 20, 1987).

Parallel cores with to high and low permeabilities were used to test the reduction of permeability in cores at residual oil saturation. Initial experiments will use 1-ft cores. Longer cores with multiple pressure transducers along the core will be used as required.

Task 4 - Prepare report on the status of the project and outline future research as required. (Start date: June 1, 1987. Completion date: July 10, 1987.)

Because of the time required for startup and obtaining industrial support, the project was delayed. The project tasks were revised to reflect an emphasis on parallel corefloods (1-ft and 4-ft long) and on parallel slim tube tests that could show in-depth permeability modification. These tests required more time than bottle tests for measurement of viscosity. An additional task (task 1, FY88) was added when industrial funding was carried over from FY87 to FY88.

Task 1 FY88 - Explore how firm or mobile is the surfactant block created by injection of the surfactant-alcohol blend. (Start date: October 1987. Completion date: January 1988.)

Because of commitments of equipment and the necessity of rebuilding the slim tubes with Monel tubing and acquisition of additional PF4, the January 1988 completion date was not achieved, and FY88 fluid injection tests were initiated in early February.

ACKNOWLEDGMENTS

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LABORATORY STUDIES

This report does not duplicate data published in the quarterly technical reports²⁻⁵ that have been submitted to the DOE nor the status report on displacement,⁶ but does supplement those discussions and provides the additional rheological data on the PF surfactants not contained in the quarterly reports.

All solutions were prepared on a weight-volume, g/100 ml basis, and viscosities of surfactant solutions were determined at various temperatures using a Brookfield LVT cone and plate viscometer and converted to a shear rate of 6 sec^{-1} for single point comparison.

Viscosity of Solutions

Viscosity scans on the PF series surfactants were conducted including salinity scans, alcohol concentration scans, temperature scans, scans in North Burbank Unit brine (NBU, 86,000 ppm TDS) and in synthetic sea water (35,000 ppm TDS composition of these brines are given in table 1). The scans showed that there are amine oxide-alcohol combinations in specific brines that yield high viscosity, as is shown in the following figures. Temperature greatly affects the viscosity, whereas there was little change with salinity over the range studied. The highest viscosities were those generated using PF7, followed by those using PF4.

TABLE 1. - Formulation of brine used in this study

<u>(Weight/Volume, g/l)</u>			
<u>Synthetic seawater</u>		<u>North Burbank Unit brine</u>	
NaCl	27.8	NaCl	66.5
MgCl ₂ •6H ₂ O	9.45	CaCl ₂ •2H ₂ O	20.27
Na ₂ SO ₄ •10H ₂ O	7.7	MgCl ₂ •6H ₂ O	5.125
CaCl ₂ •2H ₂ O	1.65		
NaHCO ₃	0.24		

Figure 1 shows an example of a PF9 amine oxide-alcohol blend that has low viscosity at high alcohol concentrations but rapidly gains viscosity as the alcohol concentration is reduced. Below a minimum ratio of amine oxide-alcohol the blend loses viscosity. Viscosity behavior shown in figure 1 is typical of amine oxide-alcohol blends with an amine oxide chain length of C_{14} . Surfactants with shorter alkyl chain lengths such as PF6 or PF3 exhibited low viscosities over a broad range of surfactant-alcohol ratios (figures 2 through 6), and no further work was pursued with these surfactants. The PF series of surfactants whose chain length is C_{14} or longer showed higher viscosities, as shown in the remaining figures. Figures 7 and 8 show the changes in viscosity for PF2 in both seawater and NBU brine salinities at ambient temperature and 50° C. Both PF1 and PF2 contain isopropyl alcohol at a ratio of about 1:1, wt:wt, and the dependency of viscosity on amine oxide (alcohol) concentration is shown in figure 9. These two surfactants were the principal materials used in parallel corefloods or parallel slim tube profile modification experiments. These surfactant alcohol blends lose viscosity as the temperature increases as shown in figure 10. Those surfactants with C_{14} chain length (PF9) are low-viscosity fluids even at ambient temperature. Longer chain PF series surfactants are viscous and are therefore often mixed with alcohols to ease handling in their manufacture.

Figures 11 and 12 illustrate the effect that amine oxide concentration has on solution viscosity. The C_{14} chain length PF9 has a lower viscosity over a wide range of concentrations as compared to PF4 which increases viscosity at relatively moderate concentrations.

Long-term stability studies in sealed bottles (figure 13) showed that PF4 became more viscous with time, whereas PF7 lost 20% of its viscosity after 30 days at ambient temperature.

Diversion Tests

The project has shown that fluids can be diverted from high-permeability zones as shown in the 1- and 4-ft parallel corefloods⁶ and in the Monel slim tube experiment.⁴⁻⁶ The last set of slim tubes were highly permeable sand packs, and diversion was achieved although the blockage was moving down the column.⁵ At high concentrations, these gels are difficult to displace, as shown when a high-concentration amine oxide-alcohol slug was injected. The

plug was essentially permanent and required a force much higher than that required to fracture the reservoir.

CONCLUSIONS

Based upon this scoping study reported in this status report (rheology) and the previous status report, NIPER-312 (fluid diversion) the following conclusions can be made:

1. Amine oxide-alcohol blends can be used to selective reduce the permeability of a more permeable core causing fluid diversion to less permeable core resulting in oil production from the tighter core.
2. Amine oxide-alcohol blends can be selected to permit the gel to be formed near the point of injection or at depth, well away from the injector.
3. Amine oxide-alcohol blends can be formulated to have low viscosity when mixed together thus permitting easy application and low horsepower to inject. As the blend(s) separate the viscosity increase, often abruptly, leaving a viscous gel to plug pores.
4. As a scoping study it has demonstrated the feasibility of the process but was not comprehensive enough to necessarily define optimum conditions.

RECOMMENDATIONS

Additional laboratory research must be undertaken to advance this scoping study and optimize the amine oxide-alcohol blends for specific applications.

1. Concentrate on one amine oxide and a series of alcohols to define propagation rate, gel strength and rheology.
2. With the same amine oxide work toward reduction in concentration from the current 30,000 ppm level.

3. Establish criteria as to how to select the blend for application at a specific salinity and temperature that will avoid development of a macroemulsion upon contact with oil.
4. Define how to place a gel at the desired distance from the wellbore i.e., that is how to control the separation of the slug.
5. Investigate the long-term stability of the gels at conditions expected within reservoirs.

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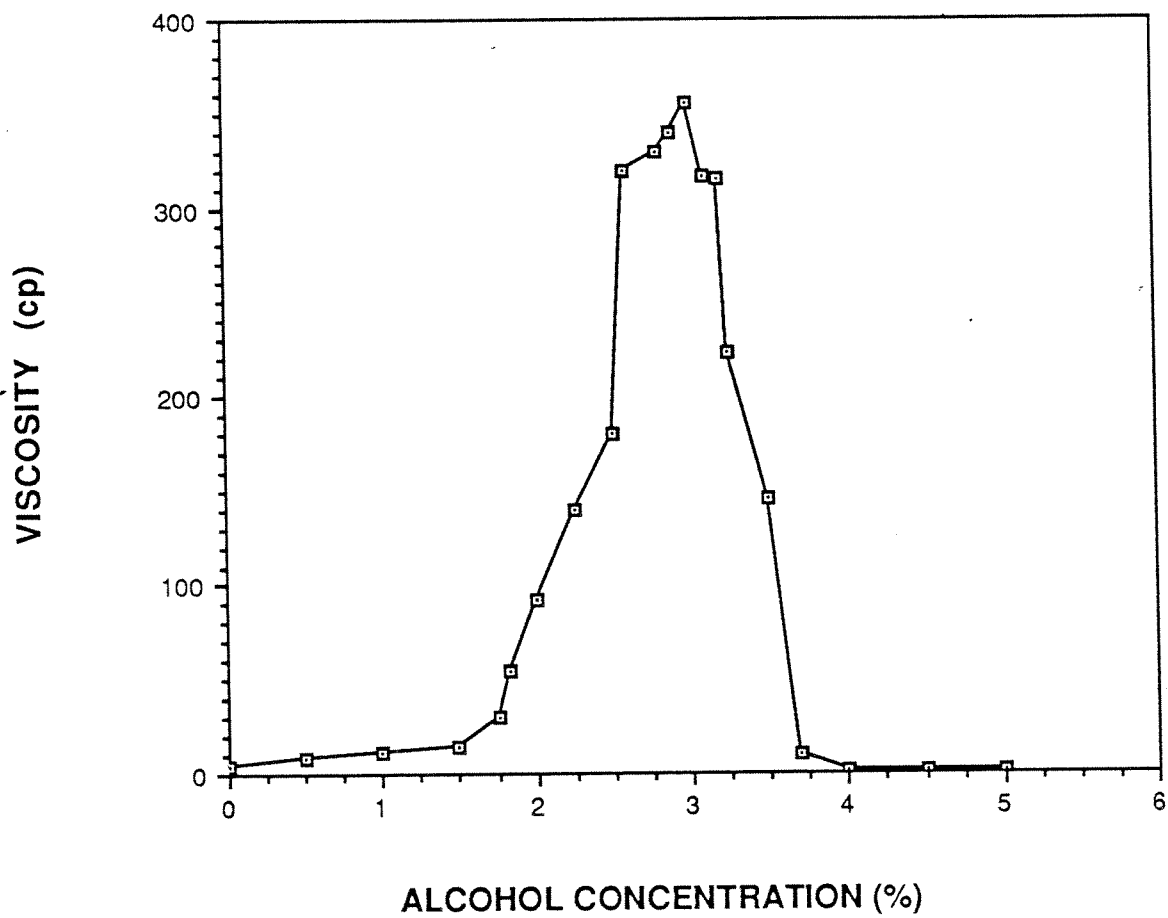


FIGURE 1. - Viscosity of 3% PF9 and isoamyl alcohol in synthetic seawater at 50° C.

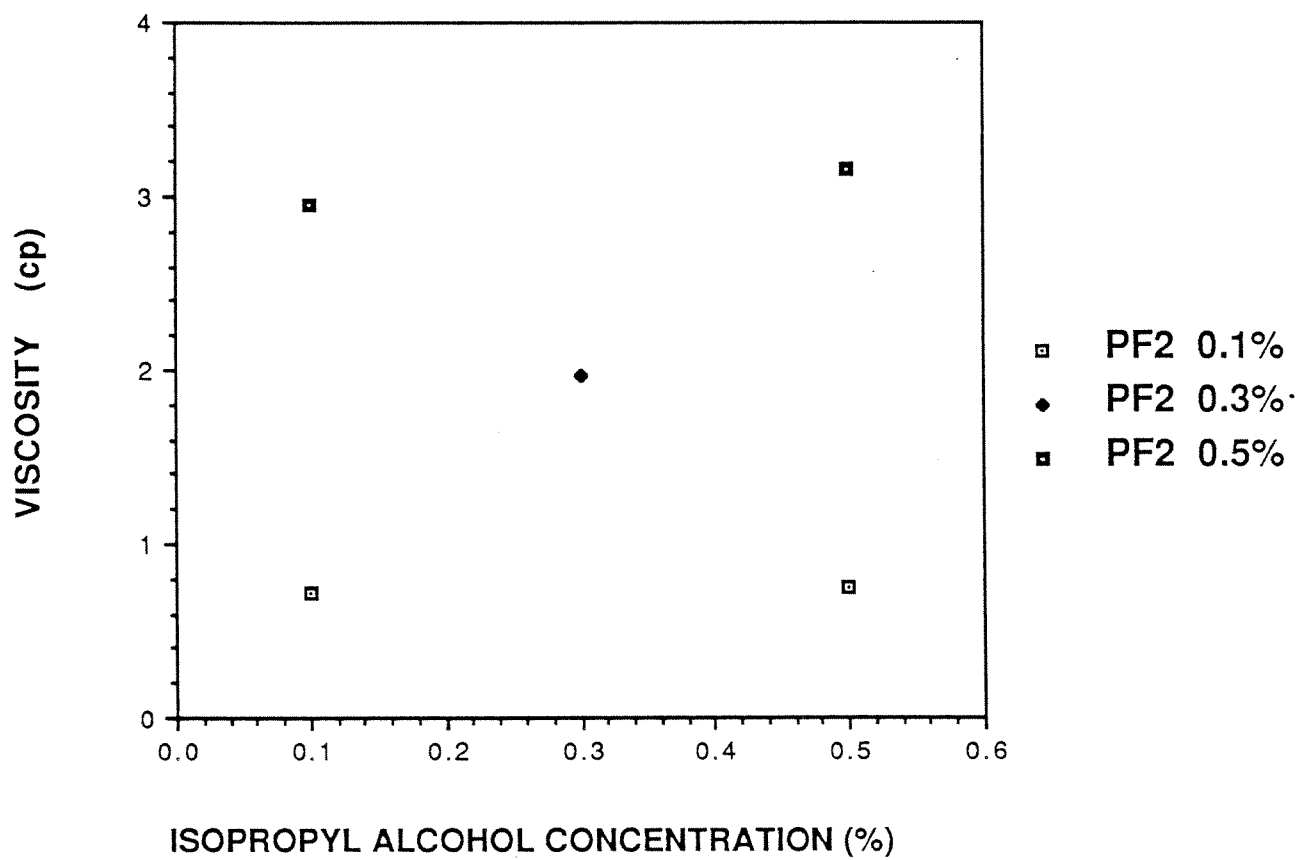


FIGURE 2. - Viscosity of PF2 and isopropyl alcohol in synthetic seawater at 50° C.

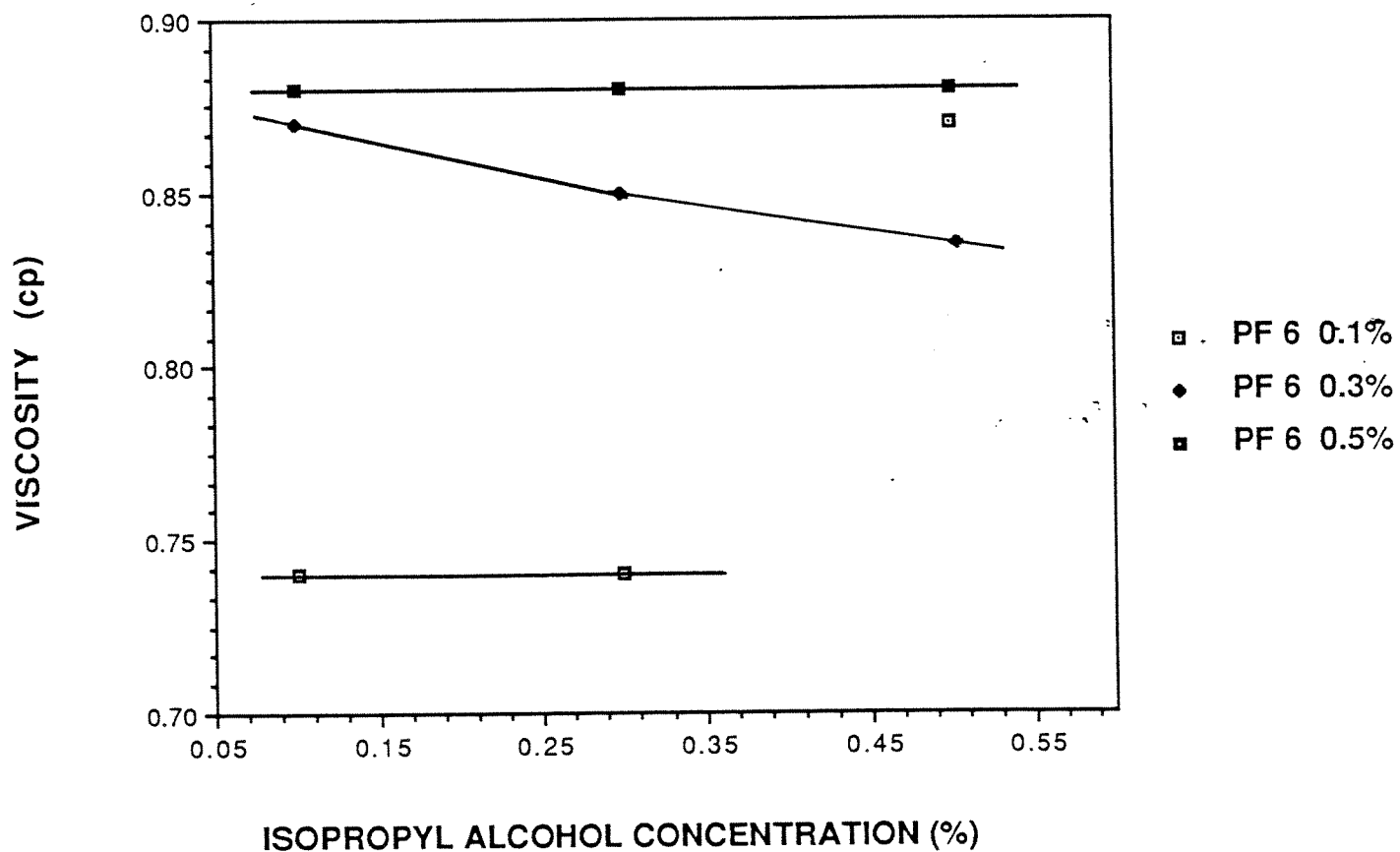


FIGURE 3. - Viscosity of PF6 and isopropyl alcohol in synthetic seawater at ambient temperature.

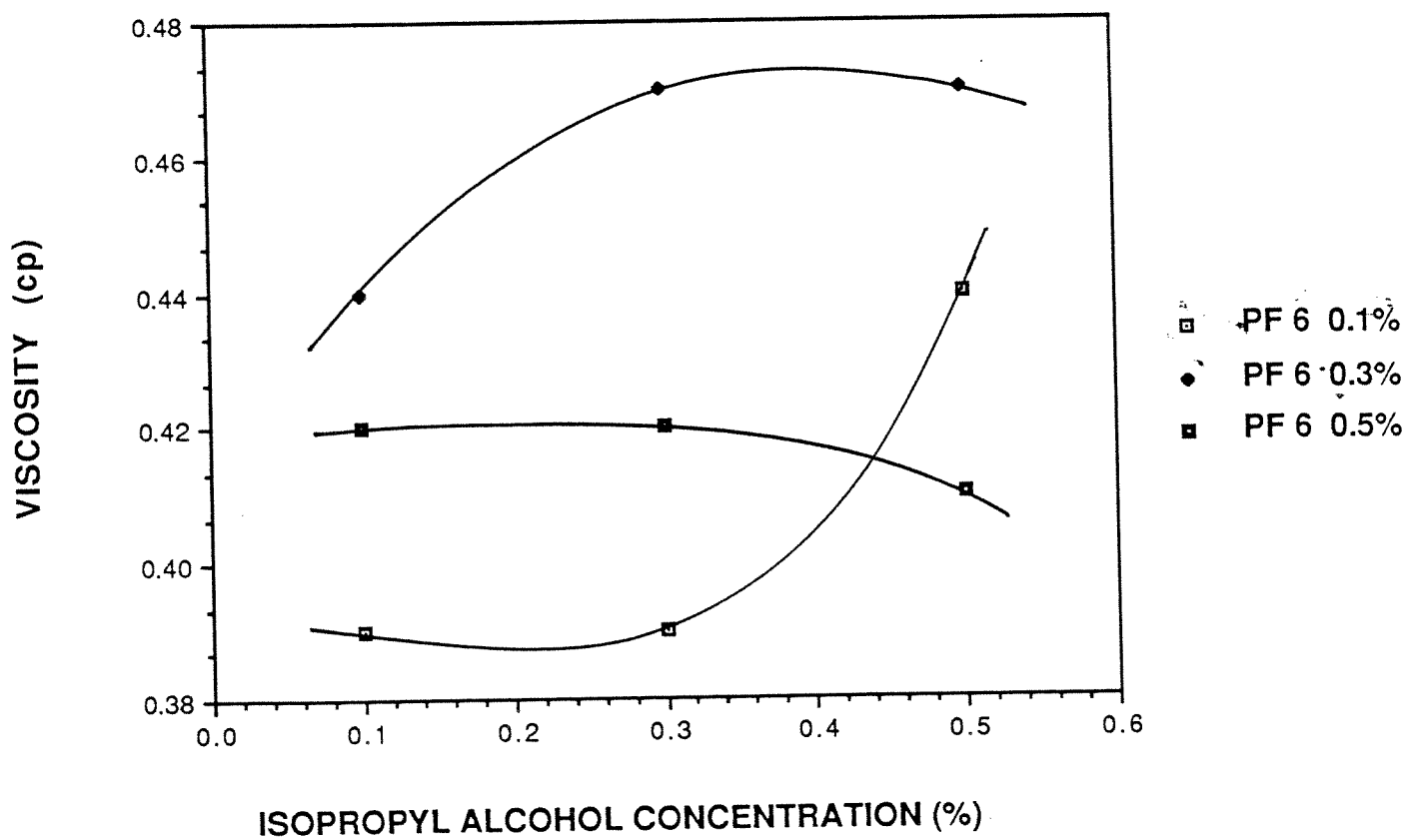


FIGURE 4. - Viscosity of PF6 and isopropyl alcohol in synthetic seawater at 50° C.

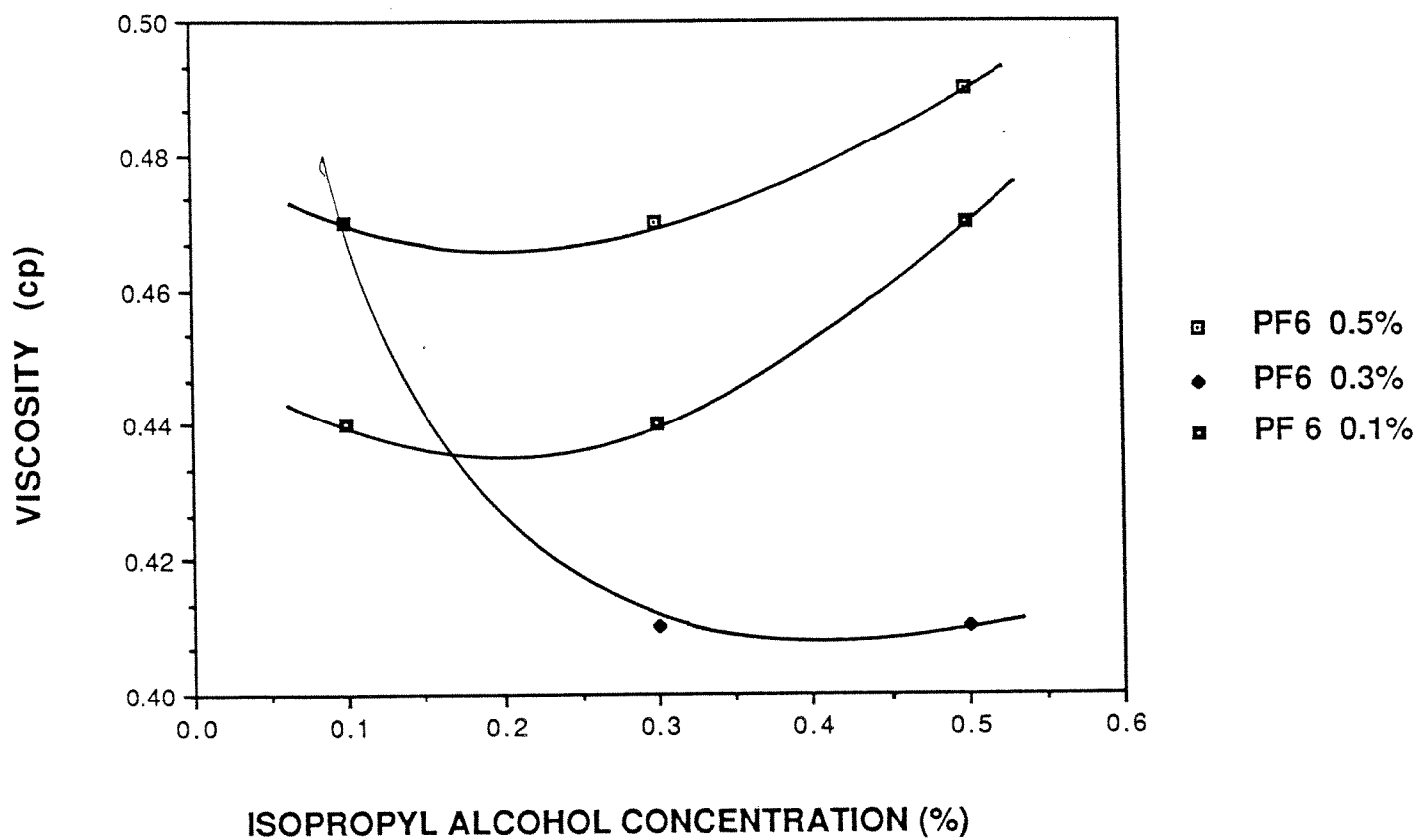


FIGURE 5. - Viscosities of PF6 and isopropyl alcohol in NBU brine at 50° C.

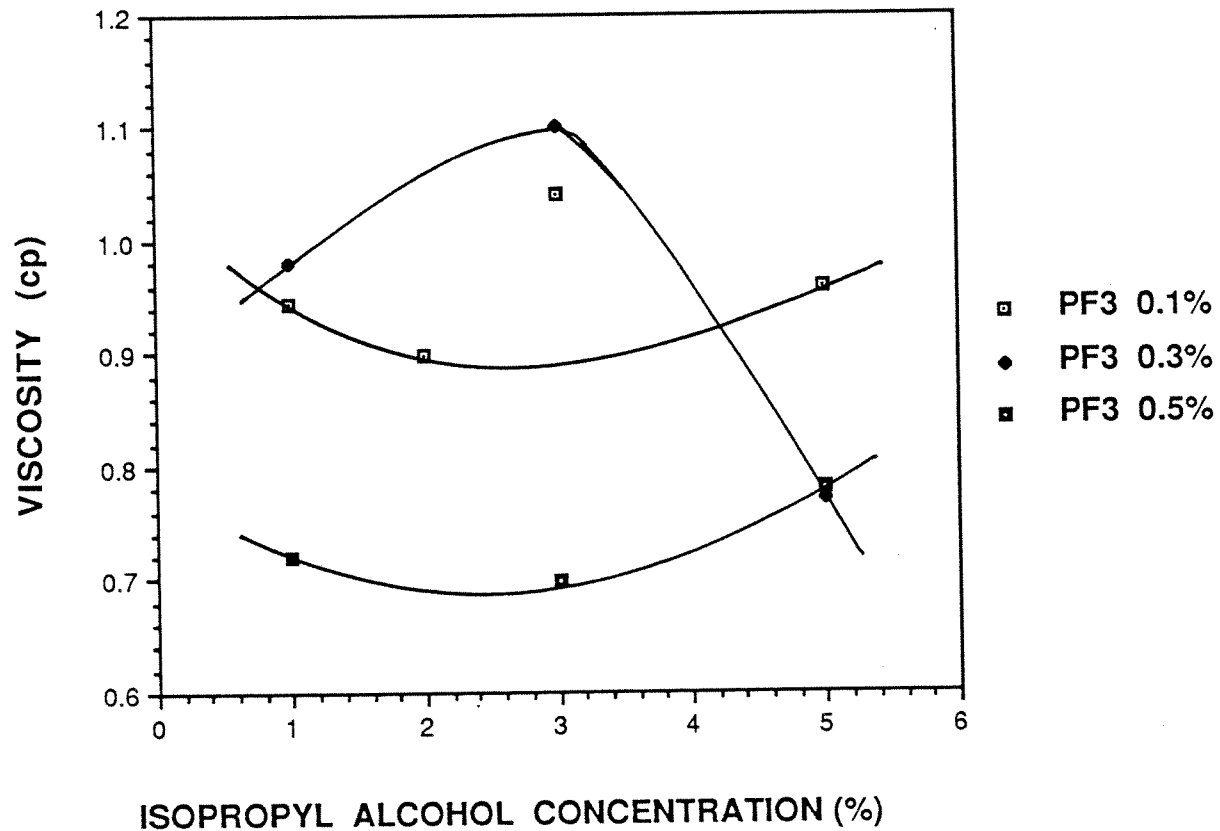


FIGURE 6. - Viscosity of PF3 and isopropyl alcohol in synthetic seawater at ambient temperature.

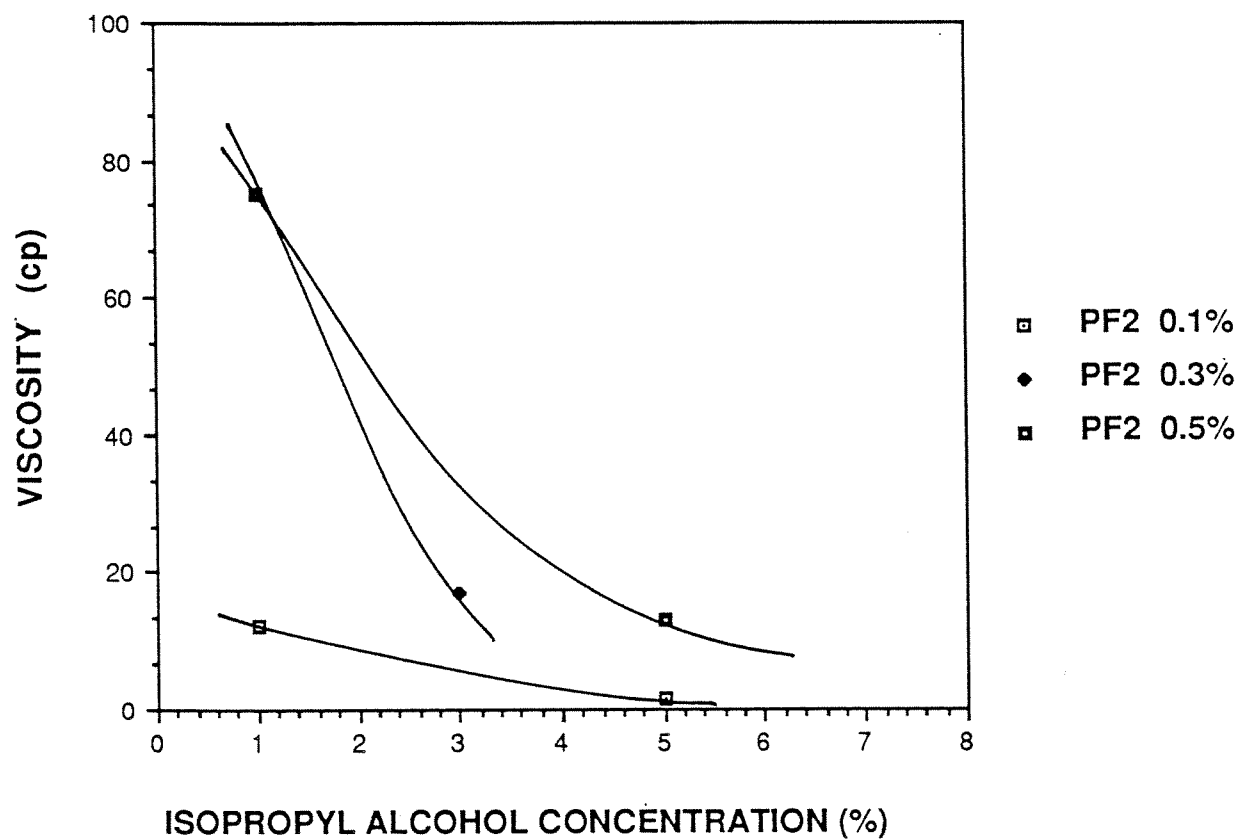


FIGURE 7. - Viscosity of PF2 and isopropyl alcohol in synthetic seawater at ambient temperature.

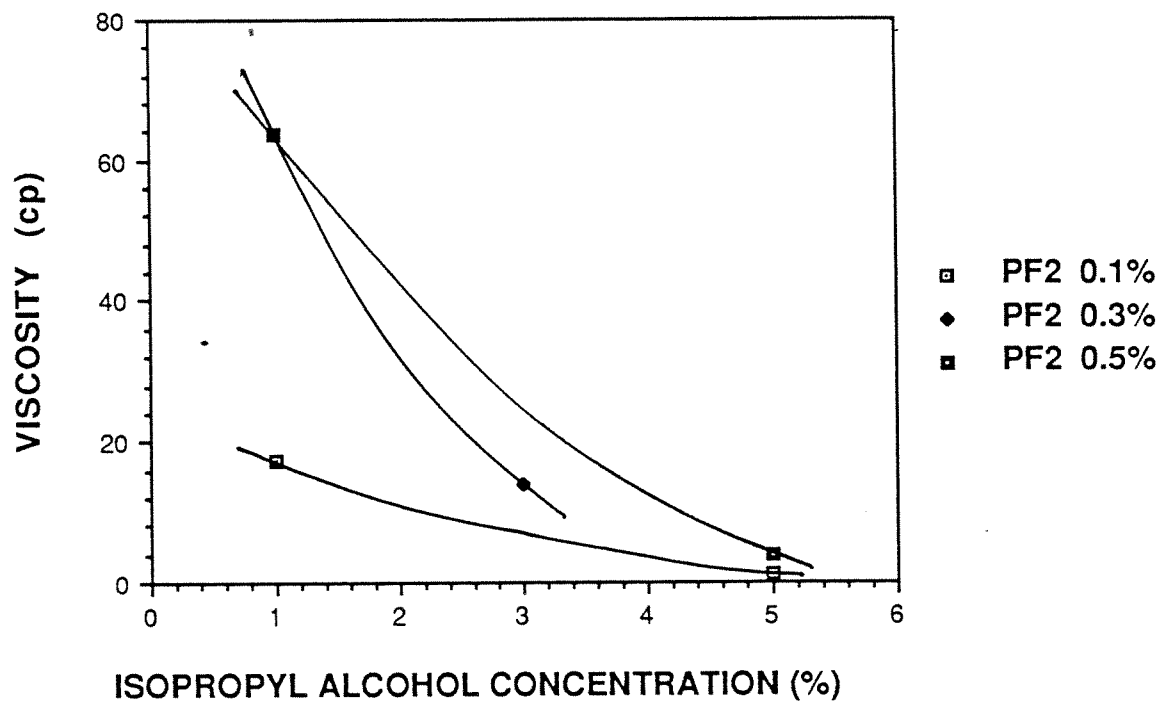


FIGURE 8. - Viscosities of PF2 and isopropyl alcohol in NBU brine at 50° C.

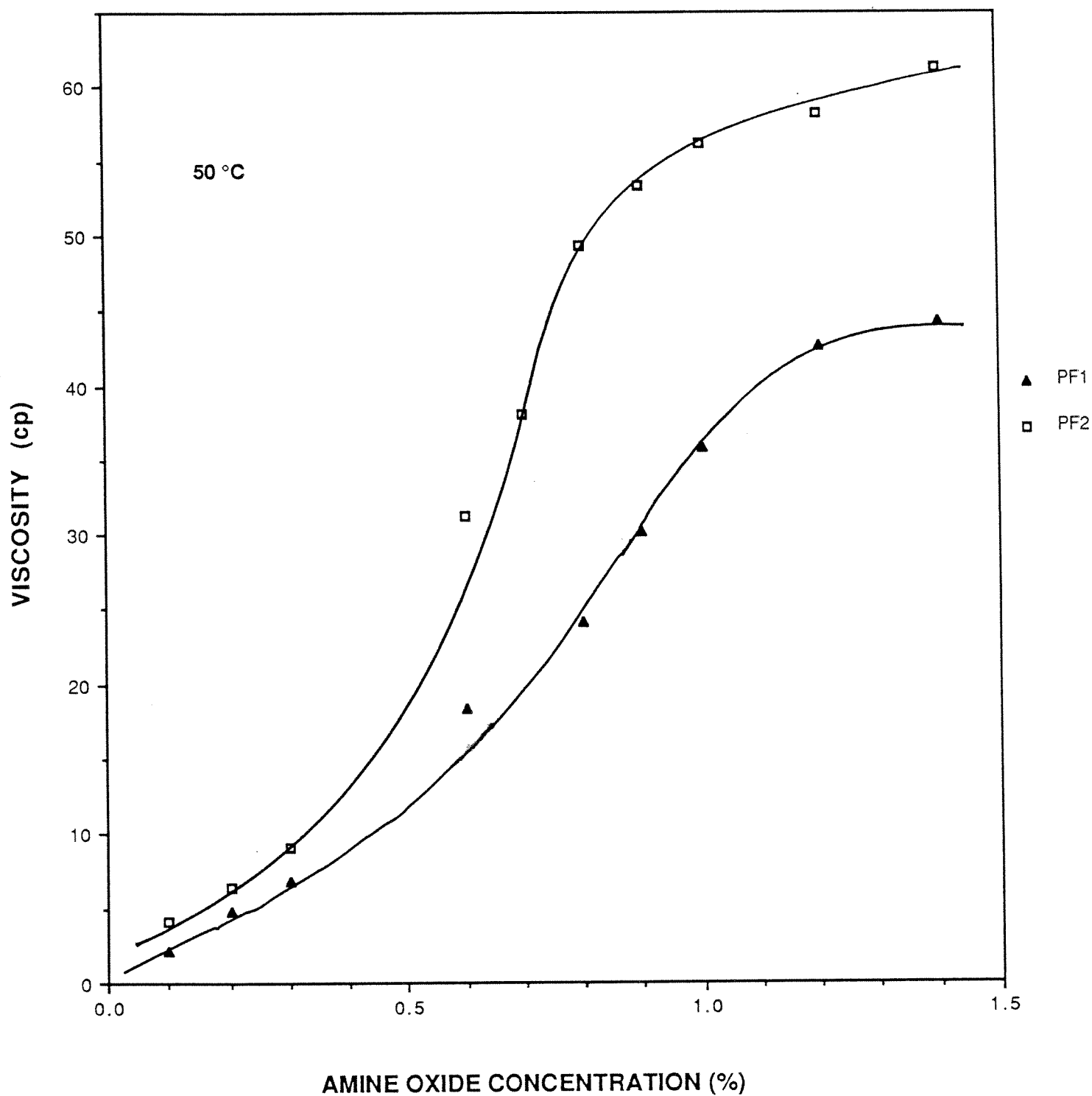


FIGURE 9. - Viscosities of amine oxides in synthetic seawater at 50° C.

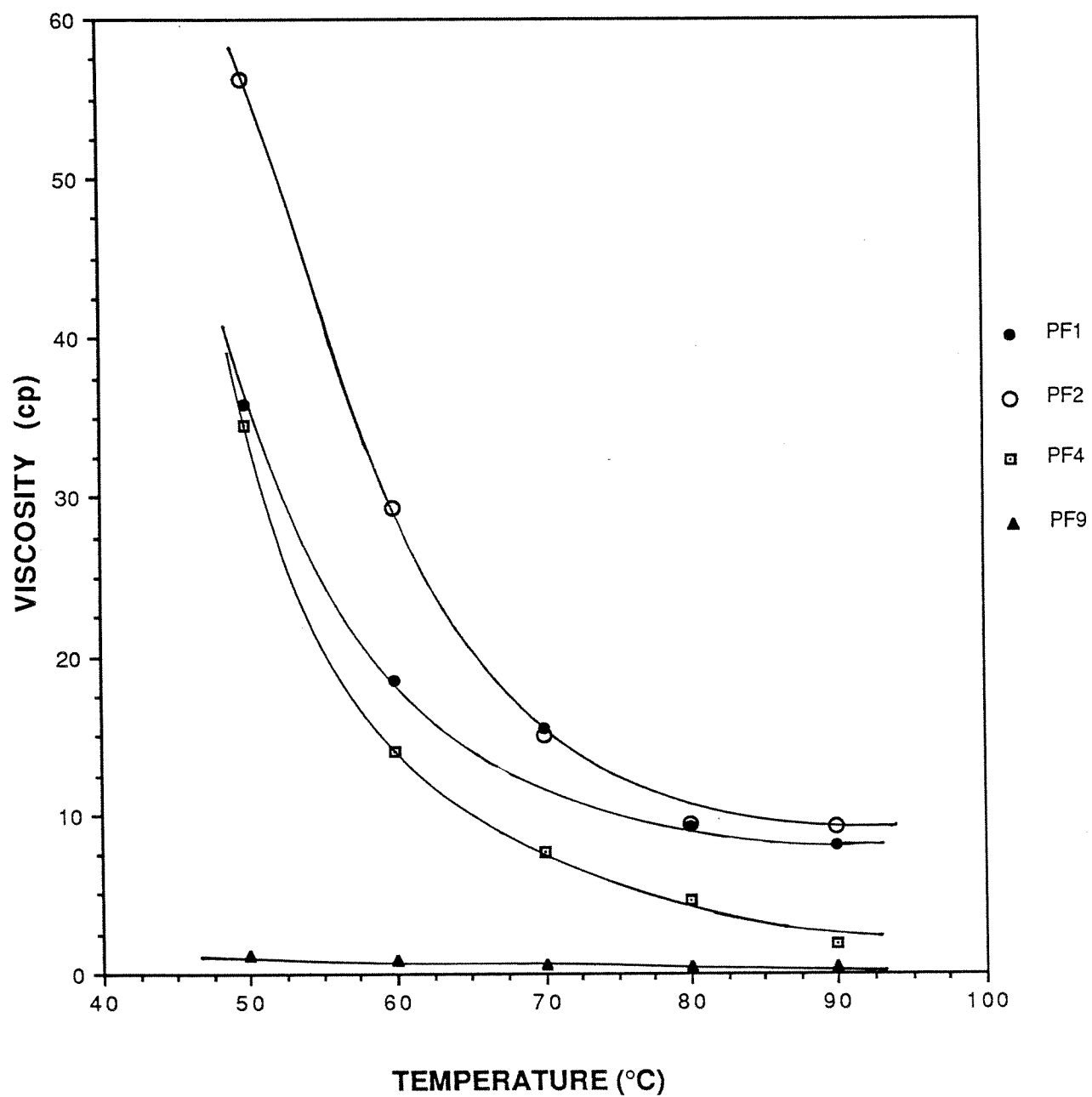


FIGURE 10. - Viscosities of 1% amine oxide in synthetic seawater at various temperatures.

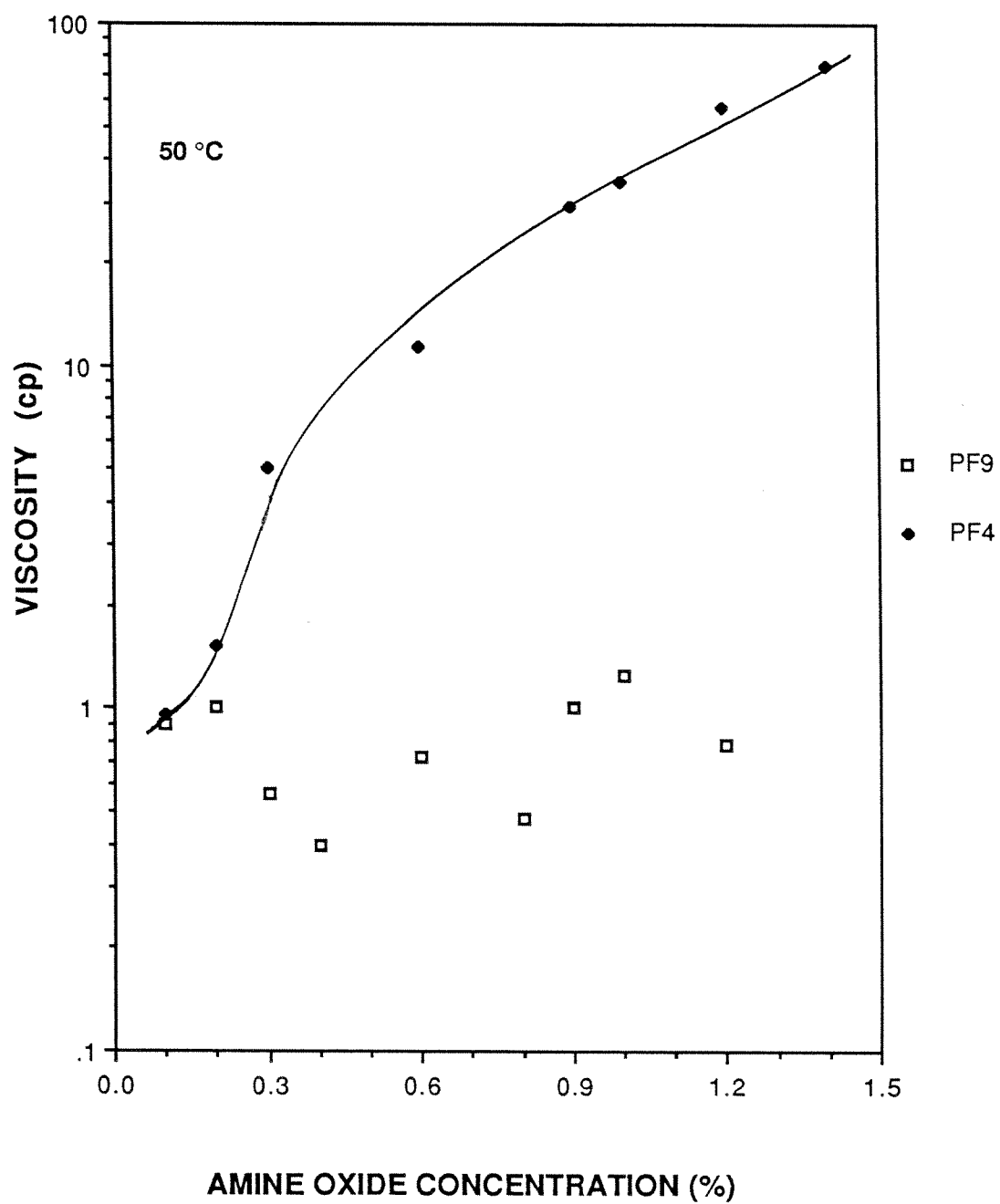


FIGURE 11. - Viscosities of amine oxides PF9 and PF4 in synthetic seawater at 50° C.

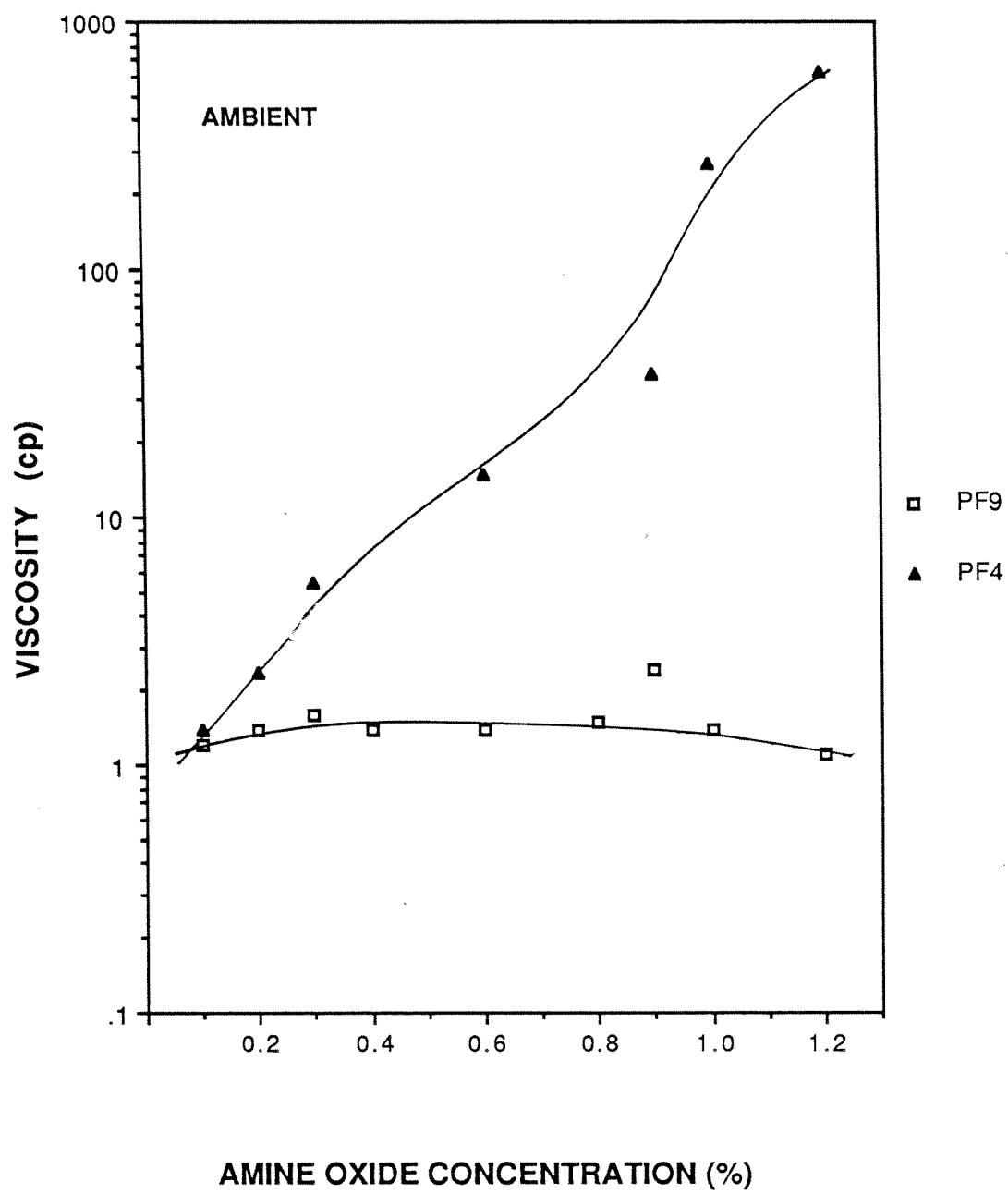


FIGURE 12. - Viscosities of amine oxides PF9 and PF4 in synthetic seawater at ambient temperature.

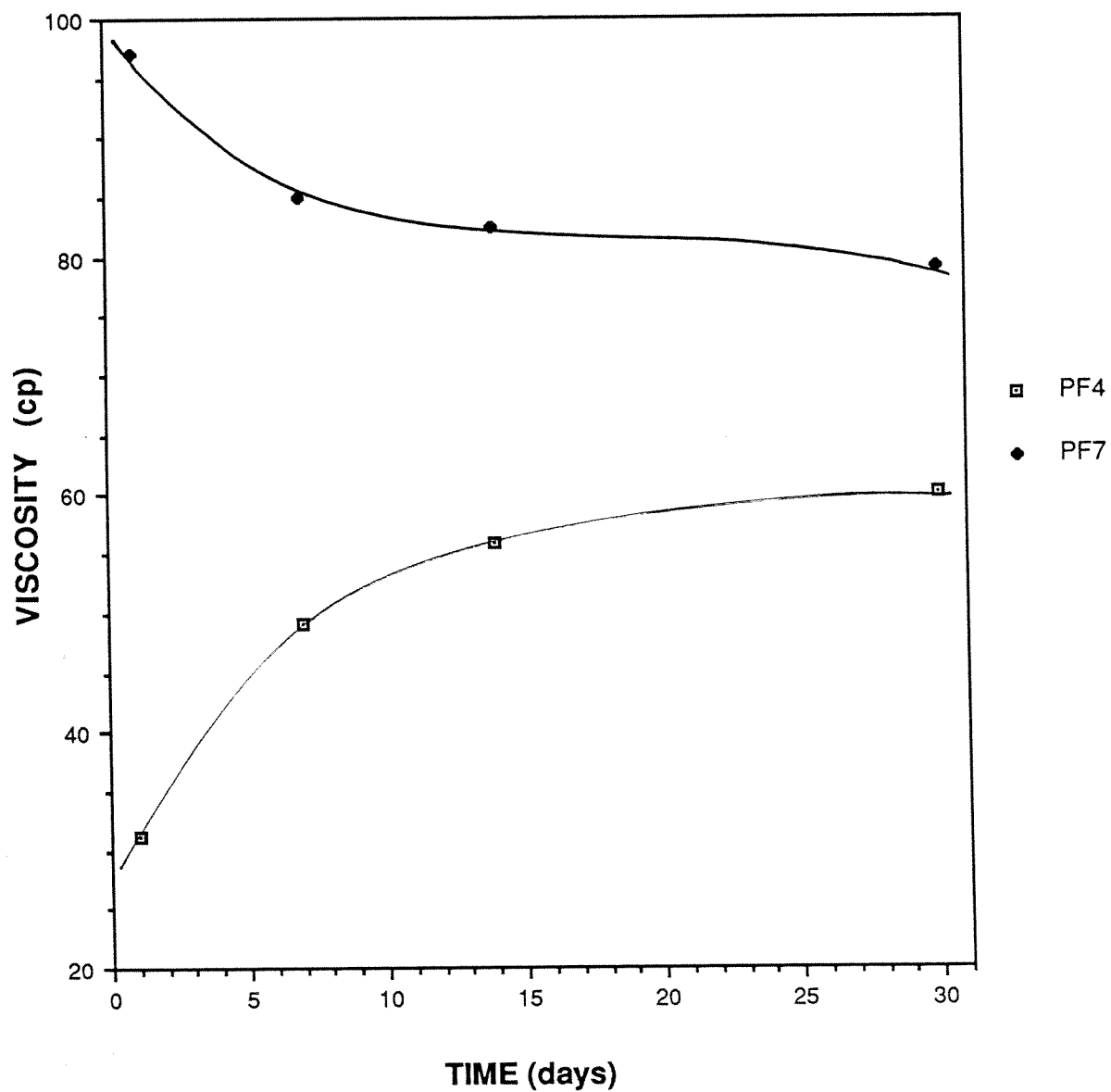


FIGURE 13. - Stabilities of 3% amine oxide (PF4, PF7)/3% isoamyl alcohol solutions in synthetic seawater at ambient temperature.

